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Reports from the Frontier: Electrifying Chemical Transformations and Separations to Valorize Wastewater Nitrogen

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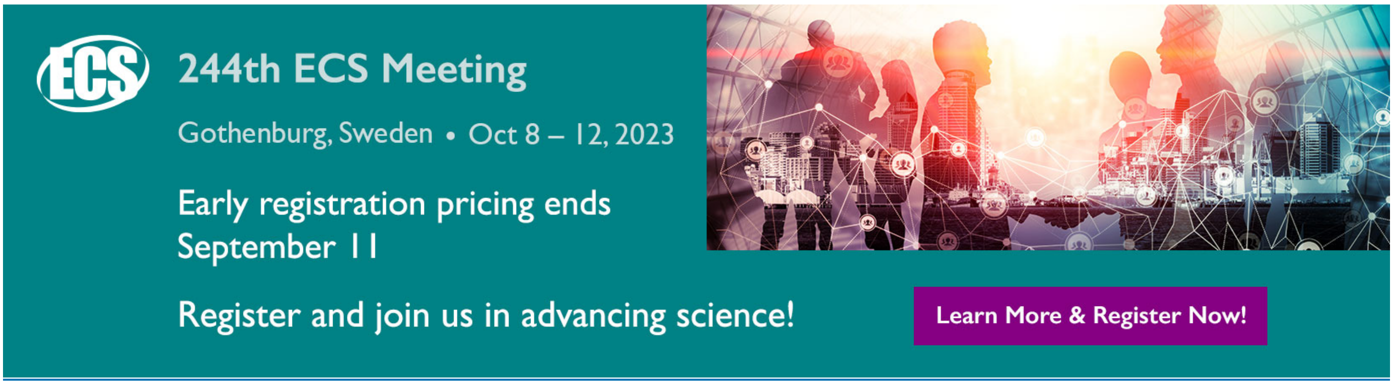

Reports from the Frontier

edited by Scott Cushing,
Interface *Contributing Editor*

This feature is intended to let ECS award-winning students and post-docs write primary author perspectives on their field, their work, and where they believe things are going. This month we highlight the work of both **Grace Lindquist**, the ETD Graduate Student Award Winner, and **Matthew J. Liu**, the IEEE Student Achievement Award Winner.

Electrifying Chemical Transformations and Separations to Valorize Wastewater Nitrogen

by Matthew J. Liu and William A. Tarpeh

Ammonia (NH_3) is an essential compound to modern society, underpinning fertilizer production and chemical manufacturing. Ammonia is also being considered as a hydrogen carrier that can be produced from renewable energy; liquified, stored, and transported readily; and utilized for energy without direct carbon dioxide (CO_2) emission.[1–3] Global ammonia demand currently exceeds 150 million tons a year (market value 70 billion USD) and is projected to increase over 2% annually.[2,4,5] Over 96% of ammonia is currently generated through the Haber-Bosch (HB) process, in which steam-reformed hydrogen (H_2) reacts with nitrogen (N_2) under reaction conditions (400–500 °C, 100–200 atm) that consume 1–2% of global energy and contribute 1.2–1.4% of anthropogenic CO_2 emissions every year.[2,5,6]

In an environmental context, ammonia is a form of reactive nitrogen. Large amounts of reactive nitrogen, such as HB ammonia, accumulate in the biosphere because 80% of wastewater globally is discharged without treatment.[7] The resulting skew in the global nitrogen cycle leads to imbalanced ecosystems and threatens water quality; damages from reactive nitrogen emissions to freshwater alone (including algal blooms and drinking water pollution) cost billions of dollars annually in the United States.[8,9] Conventional water treatment removes reactive nitrogen by converting it to N_2 (biological nitrification–denitrification); at HB facilities, the N_2 is then cycled back to produce ammonia. Directly valorizing reactive nitrogen in waste streams would shortcut the use of N_2 as an intermediate in water remediation and ammonia production, allowing savings in energy, emissions, and costs. Indeed, treating nitrogen as a resource to recover rather than simply a pollutant to remove aligns with the US National Academy of Engineering's call to manage the nitrogen cycle, a challenge central to chemical manufacturing and ecosystem protection.[10–12]

Two forms of reactive nitrogen dominate aqueous nitrogen emissions: ammonium (NH_4^+) and nitrate (NO_3^-). In the context of ammonia recovery, wastewater ammonium can be recovered through processes that selectively separate it from other wastewater constituents. Meanwhile, wastewater nitrate can be recovered as ammonia through a selective reduction reaction followed by a selective separation process. Catalysis has traditionally preceded separations in chemical manufacturing schemes, with the two processes being viewed and developed separately.[13,14] Use of impaired feedstocks such as wastewaters has created new opportunities to co-locate selective reactions with selective separations.[15–20]

We define a reactive separation process as an integration of reaction and separation imposed at the system, unit process, or molecular scale, with a particular focus on the unit process scale in this report. Reactive separations can enhance process intensification, process control, and energy consumption in wastewater treatment and valorization. Electricity provides a tunable driving force for reactive separation processes: potential differences control the free energy changes in the electrochemical system while the current controls the electrochemical reaction rate.[21] As a result, electrochemical processes enable thermodynamic and kinetic control over multiple length and time scales. In addition, electrochemical processes can be implemented in decentralized settings, which may complement the often-decentralized nature of water treatment and nitrogen pollution. For these reasons, we anticipate that electrochemists and electrochemical engineers can uniquely and meaningfully contribute to nitrogen use practices—both separations and reactions.

Electrochemical Separation Approaches

Selective separations demix solutes using driving forces such as temperature, pressure, and electrochemical gradients.[13] Fig. 1 shows electrochemical stripping, a process that uses electrochemical driving forces to recover >93% of wastewater NH_3 based on charge and volatility. Ammonium-rich wastewater is fed into the anode chamber (left chamber). The anode and cathode chamber are separated by a cation exchange membrane to allow electromigration of ammonium into the cathode chamber. The catholyte basifies to an alkaline pH (typically 10.5–11.5) that can be tuned through the applied current, thereby avoiding the need for direct chemical input (e.g., of sodium hydroxide to basify the solution). As a result, ammonium deprotonates to ammonia ($pK_a \sim 9.25$), which is a volatile species. Over time, high ammonia vapor pressure builds up in the cathode chamber. The cathode and trap chamber are separated by a hydrophobic gas permeable membrane (e.g., polypropylene) to allow volatilized ammonia to diffuse to the trap chamber for collection. For example, sulfuric acid can be used such that high-purity ammonium sulfate, a commodity fertilizer, is generated.[22–25] Traditionally, ammonia stripping has been employed to treat ammonium-rich wastewater. The treatment process is predicated on

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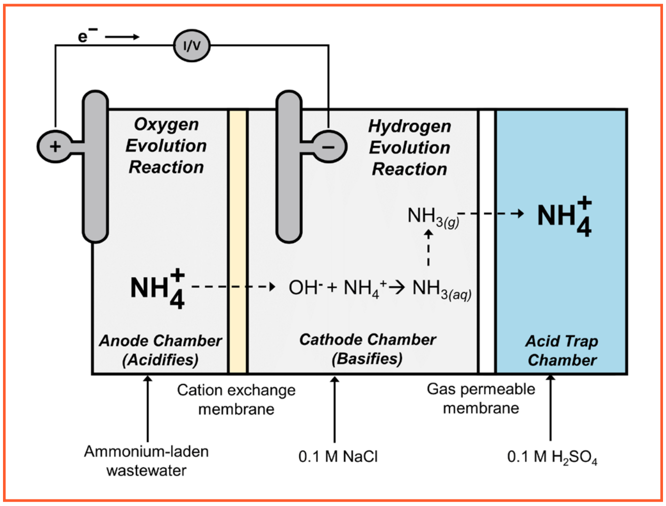

Fig. 1. ***Electrochemical stripping reactor.*** *A cation exchange membrane separates the anode and cathode chamber, and a gas permeable membrane separates the cathode and trap chamber. Hydrogen evolution in the cathode chamber produces an alkaline environment, allowing ammonia to diffuse across the gas permeable membrane into the trap chamber. Ammonia in the trap chamber protonates to ammonium, maintaining an ammonia concentration gradient between the cathode and trap chambers.*

the need for centralized infrastructure that collects wastewater for treatment. However, wastewater is often generated and collected in a distributed fashion, creating a need for self-sufficient processes such as electrochemical stripping that can treat water on-site while generating ammonia in a distributed manner. Electrochemical membrane reactors such as electrochemical stripping can therefore act as reactive separations platforms to recover high-purity ammonia from ammonium-rich wastewaters and/or nitrate-rich wastewaters.

Electrochemical Reaction Approaches

Electrocatalysts mediate the transfer of electrons through a catalyst active site, enabling electrochemical redox reactions to occur with increased reaction rate, energy efficiency, and/or product selectivity.[26] Implementation of an ammonia-selective nitrate reduction reaction (NO_3RR) catalyst in the cathode chamber of electrochemical stripping could allow simultaneous water treatment and electrified ammonia manufacturing.

$$NO_3^- + 8e^- + 9H^+ \rightarrow NH_3 + 3H_2O$$

NO_3RR electrocatalysts consist largely of heterogeneous, metallic catalysts such as single metals (e.g., Pt, Pd, Cu, Ti),[27,28] alloys (e.g., CuNi, PtRu),[29,30] and core–shell nanoparticles (e.g., Ru–oxygen-doped-Ru, Cu/CuO_x–Co/CoO).[31,32] However, the surface structures of these electrocatalysts are difficult to control at an atomic level and they tend to restructure under reaction conditions, making it challenging to isolate the contributions of different surface species to reactivity. For example, titanium, an inexpensive and abundant metal, has been identified as a robust electrocatalytic material for NO_3RR.[28] The reasons underlying the catalytic performance of titanium remain unclear, especially regarding the role of near-surface titanium hydride (TiH_x, $0 < x \leq 2$), a water-stable titanium species that electrochemically forms under protic, reducing conditions.[33]

We overcame the obstacle of linking catalytic performance with surface structure by combining systematic synchrotron X-ray characterization of Ti electrodes with electrochemical testing (Fig. 2). Through ex situ grazing-incidence X-ray diffraction (GIXRD) and total electron yield X-ray absorption spectroscopy (TEY XAS) measurements, we demonstrated that near-surface TiH_2 formation begins at NO_3RR potentials $\leq -0.4V_{RHE}$ and that TiH_2 dominates near-surface speciation $\leq -0.8V_{RHE}$. For a fixed applied potential, increasing NO_3RR duration promotes near-surface TiH_2 formation, though to a lesser extent than varying the potential. These results informed an electrochemical treatment method of Ti to produce TiH_2/Ti electrodes. Controlled potential electrolysis of unamended Ti electrodes vs. TiH_2/Ti demonstrated that at all the tested potentials (−0.4, −0.6, −0.8, and −1.0 V_{RHE}), the rate-determining and selectivity-determining steps of NO_3RR were unaffected by the initial near-surface structure.[34] These findings therefore helped decouple hydride formation from NO_3RR performance under a variety of reaction durations and applied potentials, which are parameters that may need to be varied to formulate different value-added products on-demand and to remove pollutants to threshold values. In a follow-up study, we found that mass transport effects on interfacial electrolyte pH and solute concentrations played a more impactful role than near-surface structure in regulating NO_3RR activity and selectivity.[35] The influence of electrolyte properties on NO_3RR was especially salient to the context of water treatment, which involves the need to accommodate various wastewater compositions.

Outlook

Ammonia synthesis in the 21st century will be a multifaceted effort that needs to fulfill several goals relating to energy, the environment, and resource equity. First, methods of ammonia synthesis must be increasingly coupled with renewable energy. For example, ammonia could be produced in electrolysis cells powered by electricity from solar or wind energy. According to the US Department of Energy (DOE), electrochemical technologies must operate at current densities >300 mA cm^{-2} while maintaining energy efficiencies >60% and faradaic efficiencies >90% to be economically viable options for carbon-neutral fuel production (fuel energy cost <\$0.3 kWh^{-1}).[36] Current state-of-the-art electrochemical ammonia synthesis systems, whether by N_2 by NO_3^- reduction, can typically achieve one or perhaps two of these metrics,[4,37,38] but rarely all three. The technology readiness level (TRL) of electrochemical ammonia synthesis remains at an estimated TRL 1–3,[5] meaning that the most mature technologies remain experimental proofs of concept. Substantial work at the intersection of electrocatalyst and electrochemical engineering research, design, and scale-up will help guide electrochemical technologies toward achieving the metrics prescribed by the DOE.

The second goal of 21st century ammonia synthesis is to respond to quality-of-life needs, especially in the context of resource equity. The infrastructure needed for HB production plants requires large capital investment, which favors economies of scale.[36] As a result, HB production plants are concentrated in North America and in Western Europe, leading to inequitable distribution and pricing of HB ammonia

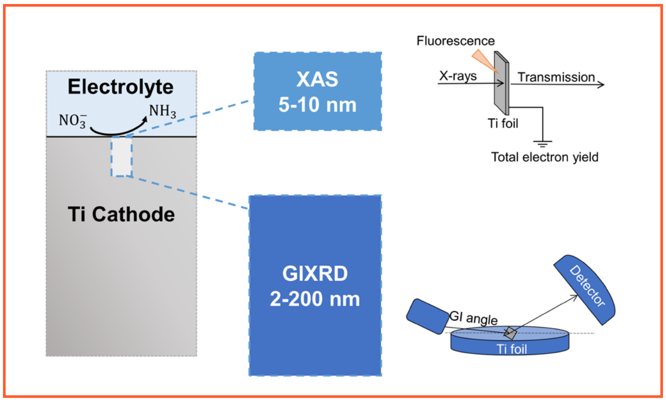

Fig. 2. ***Ex situ synchrotron X-ray characterization of the titanium electrode near-surface.*** *Grazing-incidence X-ray diffraction (GIXRD) characterizes the long-range, crystalline structure of the near-surface while X-ray absorption spectroscopy (XAS) gives insight into the short-range, local Ti coordination environment of the near-surface (e.g., coordination number and interatomic distance). We developed quantitative relationships between near-surface titanium hydride content and various NO_3RR durations and applied potentials, allowing us to better decouple the formation of titanium hydride from NO_3RR performance. Adapted with permission from M. J. Liu et al.,* J. Am. Chem. Soc., ***144****, 5739–5744 (2022). © 2022 American Chemical Society.*

around the world.[39] Electrochemical methods of ammonia synthesis can enable distributed manufacturing of ammonia, where modular process units can leverage distributed feedstocks to deliver products at the source. In this way, technological and economic barriers to accessing ammonia as a resource can be lowered.

The third goal for 21st century ammonia synthesis is to address rather than exacerbate environmental remediation. As we discussed in this report, NO_3RR represents an avenue through which water can be simultaneously treated with ammonia generation and recovery. Wastewater can be utilized as a feedstock beyond NO_3RR to enable transformations of inorganic nitrogen across the entire oxidation state of nitrogen.[40] We envision that fugitive reactive nitrogen emissions of all forms can be converted to high-purity ammonia and recovered, or vice-versa. Such flexibility would allow wastewater to transition from being a waste stream to a valuable feedstock from which tunable and on-demand methods of chemical manufacturing can be utilized to mine the water for maximal value before discharge.[13]

In his Nobel Prize acceptance speech in 1919, Fritz Haber said of his ammonia synthesis process: "It may be that this solution is not the final one."[41] Indeed, the science, technology, economics, policy, and equity surrounding ammonia synthesis and nitrogen management will continue to evolve in the 21st century. Amidst these multifaceted changes, electrochemists and electrochemical engineers are uniquely positioned to contribute to the opportunities of coupling ammonia synthesis with nitrogen management.

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Honors and Awards: Professor Tarpeh is a recipient of the *Forbes* 30 Under 30 Award (2019), *Chemical & Engineering News* Talented 12 Award (2019), Camille Dreyfus Teacher Scholar Award (2022), and Electrochemical Society Toyota Young Investigator Award (2022).

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